

APPENDIX P

Limiting Factors for Phytoplankton Growth and Yield in the San Luis Drain

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Abstract

Phytoplankton blooms have been extensively studied and modeled in eutrophic estuaries, lakes, reservoirs, and ponds, but factors regulating phytoplankton growth yield and growth rates (biokinetics) in eutrophic rivers are less well understood. A growing body of evidence suggests that phytoplankton biokinetics in rivers are influenced by factors other than macronutrient concentrations, such as residence time and micronutrient concentrations. In this study, we investigated phytoplankton biokinetics in a nutrient enriched drainage in the Central Valley of California over a three year period. Despite nitrate (13 mg-N L^{-1}) and phosphate (0.2 mg-P L^{-1}) concentrations exceeding up to fifty-times kinetic half-saturation concentrations and saturating sunlight conditions ($720 \text{ langleys d}^{-1}$), phytoplankton rarely exhibited maximal growth rates. Only in one instance did the observed growth rate reach the estimated maximum growth rate of 0.06 h^{-1} . Analysis of field observations using a mechanistic model demonstrated that in the presence of excess nitrate and phosphate, phytoplankton growth rates were often limited by carbon dioxide availability and that mineral sediments acted as a reservoir for trace nutrients. Phytoplankton biomass reached a maximum carrying capacity ($200 \text{ mg-chlorophyll L}^{-1}$) after approximately 60 hours of residence time. Growth yield was limited by a combination of phosphate depletion and zooplankton grazing.

Keywords

phytoplankton, growth rate, growth yield, nutrient limitation, algae growth model, biokinetics, San Joaquin River, Central Valley

Abbreviations and Notations

| | | | |
|------------|--|-------------|--|
| SLD | San Luis Drain | μ_{max} | maximum growth rate |
| N_t | concentration of phytoplankton at time t | g_{max} | maximum grazing rate |
| N_0 | concentration of phytoplankton at time 0 | K_{sm} | mineral solids half-saturation constant |
| K | carrying capacity | K_{sp} | phosphate half-saturation constant |
| r | observed growth rate | K_{sc} | carbon dioxide half-saturation constant |
| t | elapsed time | K_{sz} | zooplankton grazing half-saturation constant |

Introduction

Eutrophication of surface waters has been a recognized environmental problem for over forty years (Hutchins, 1973; Levin, 1967). Although phytoplankton are the foundation of many aquatic food-webs, the excessive growth of phytoplankton in eutrophic waters can have a significant negative impact on habitat quality and some phytoplankton can be directly toxic to fish and wildlife (Haider et al., 2003; Scavia and Bricker, 2006). Accumulation of phytoplankton biomass and subsequent phytoplankton population crashes can cause anoxic conditions in rivers, lakes and estuaries (Billen et al., 2001; Hagy et al., 2004; Jassby and Nieuwenhuys, 2005; Jorgensen, 1976; Parr and Mason, 2004; Pers, 2005; Scavia and Bricker, 2006) and high phytoplankton concentrations reduce other beneficial uses by contributing foul tastes, offensive odors and formation of disinfection-by-product precursor compounds (Nikolaou and Lekkas, 2001; Sladeckova, 1998; Wnorowski, 1992).

Phytoplankton blooms, and subsequent negative impacts, have been extensively studied and modeled in estuaries, lakes, reservoirs, and ponds (Billen et al., 2001; Bowie et al., 1984; Cerco and Noel, 2004; Hilton et al., 2006; Jorgensen, 1976; Koelmans et al., 2001; Nyholm, 1978; Pers, 2005). The factors limiting the biomass yield of phytoplankton in confined waterbodies and estuaries are typically attributed to macronutrients: nitrogen and phosphorous, but growth rates can be controlled by any number of factors, including light availability, micronutrient limitation, and zooplankton grazing (Knowlton and Jones, 1995; 1996; Koch et al., 2004; Kuuppo et al., 1998; Robson, 2005; Wu and Chou, 2003). Enclosed systems are well enough understood that robust phytoplankton biokinetic models have been developed for lakes and reservoirs to describe the interactions between algal growth, algal yield, light availability, grazing, and nutrient concentrations (e.g. Bowie et al., 1984; Cugier et al., 2005; Hilton et al., 2006; Pers, 2005; Plus et al., 2006).

Phytoplankton growth in eutrophic rivers is less well understood (Hilton et al., 2006). A growing body of evidence suggests that phytoplankton growth in rivers is strongly influenced by physical factors, such as residence time and mixing rates, and that these and other physical factors may be as important as macronutrient concentrations in regulating phytoplankton growth yield and growth rates (biokinetics).

The objective of this study was to identify fundamental process controlling algal biokinetics in a highly eutrophic river. The limits of phytoplankton biokinetics were examined in a concrete-lined river in the Central Valley of California which conveys nutrient rich agricultural drainage. High nutrient conditions, combined with abundant sunlight and warm temperatures, results in significant summer phytoplankton blooms and presents an opportunity to study factors limiting algal growth in the presence of excess macronutrients. Phytoplankton growth was measured in the river and environmental conditions were related to phytoplankton biokinetics using statistical methods and a mechanistic model. The mechanistic model identified limiting factors for growth and yield and suggested that suspended sediments have a stimulatory influence on diatom growth and function as a source of nutrients as dissolved nutrients are depleted.

Methods

Lagrangian studies were conducted in the San Luis Drain (SLD) over a three year period (2003 to 2005). Samples were collected at each of the 18 hydraulic checks along the 43 km study area as well as at the entrance and exit of the channel (Figure 1). Chemical and physiological measurements were made at the up-stream side of each check and grab samples were depth integrated. Flow was measured continuously at the head and exit of the channel. Residence time in the drain as a function of distance was measured by velocity and dye studies and confirmed by hydraulic calculations based on design specifications. The distance along the drain was related to residence time and data was analyzed as a function of residence time. Phytoplankton growth and water quality changes were measured in May 2004 and January 2005 and two times each in June and July 2003 and 2004. Phytoplankton biokinetic pattern in the drain was measured again in June 2005 to confirm that June year to year results were comparable.

Field measurements were made with handheld sondes and water quality measurement devices, including a YSI 6600 sonde, HACH turbidometer, and Myron combination Ultraprobe. For dye studies, Hydrolab combination sondes were used. Handheld probes were calibrated daily before each use. Stream velocity was measured using a Marsh-McBirny velocity probe. Confirmation (QC) of continuous measurements was performed using replicate sampling for laboratory analysis and duplicate calibrated instruments, as required. Measurement of incident photosynthetically active radiation (PAR) and PAR attenuation with depth in the SLD were made using quantum light detectors (LiCor, Lincoln, NE). Photozone was defined as the depth where light penetration was 2% of incident light.

Samples collected in the field were transported to Berkeley National Laboratory for analysis. All analyses were run within the allowed holding time applicable to the preservation method used (American Public Health Association, 1998). Total organic carbon (TOC) was measured by high temperature combustion according to Standard Method (SM) 5310 B (American Public Health Association, 1998). Dissolved organic carbon was measured on split samples after filtration through a GF/F glass fiber filter by the same method. Total suspended solids (TSS) and volatile suspended solids (VSS) were analyzed by SM 2540 D and E, respectively. Mineral solids (MS) was calculated as TSS minus VSS. Chlorophylls (chl-*a*, chl-*b*, chl-*c*), pheophytin-*a* (pha-*a*), and xanthophyll were extracted and analyzed according to SM 10200H (American Public Health Association, 1998).

Ortho-phosphate was determined on samples filtered through a glass-fiber filter (0.7 micron). Ortho-phosphate and total phosphorous were quantified by the Ascorbic Acid Method (adapted from SM 4500-P-E). Total phosphorus was determined on non-filtered samples following persulfate digestion. Total iron was determined by the Phenanthroline Method (SM 3500-Fe B) (American Public Health Association, 1998).

The algal community was characterized by measurement of phospholipid fatty-acid (PLFA) profile. To extract PLFA from suspended algae and detritus, 500 ml of water sample was filtered through a Whatman GF/F glass fiber filter within 24 hours of collection. The filter was placed in a 25 mm glass tube and stored at -20 °C until extraction. The total lipids are extracted from the filter with a modified Bligh-Dyer

solution which consists of 5 ml of chloroform, 10 ml of methanol, and 4 ml of phosphate buffer. The phospholipids are then separated from total lipids on C18 column (Unisil, Clarkson Chemical, South Williamsport, PA). Isolated phospholipids are methylated and analyzed on an Agilent 6890N Gas Chromatograph (GC) equipped with a Flame Ionization Detector (Guckert et al., 1985). Peak confirmation is accomplished on an Agilent 5972A mass spectrometer and double bond position confirmed with a dimethyl disulfide derivation (Nichols et al., 1986). Peak quantification was accomplished by use of an internal 19:0 phospholipid standard (1,2-Dinonadecanoyl-sn-Glycero-3-phosphocholine) (Avanti, Alabaster, AL) which is added immediately prior to extraction, and an external 11:0 carbon fatty acid methyl ester standard (methyl decanoate) (Matreya, Pleasant Gap, PA) which is added immediately before analysis on the GC.

PLFA recovered from water samples can be assigned to specific organism classes and biomass estimated for each class using the amount of lipid recovered. Diatom were characterized by 16:3w3 and 20:5 fatty acids; dinoflagellates by the occurrence of 22:6w3; green algae by 18:3w3; bacteria by 15:0 and 15:1; and terrestrial biomass by 25:0 and 26:0 fatty acids (Becker et al., 2004; Galois et al., 1996; Muller-Solger et al., 2002).

Weather data was collected from three stations in the Central Valley. Central Valley temperature and precipitation averages were calculated by averaging daily data for the thirty year record from Stockton, Merced and Los Banos, CA. Weather clarity (number of clear days) was calculated from the 30 year Stockton record only.

Experimental data were fit to the logistic population model using Grapher software (Golden Software, Golden, CO). The Logistic model is used to describe resource limited biokinetic relationships:

$$N_t = \frac{K}{1 + \left[\frac{K - N_o}{N_o} \right] e^{-rt}} \quad \text{Eq. 1}$$

where N_t is the concentration of phytoplankton at time t , N_o is the initial concentration of phytoplankton, K is the maximum phytoplankton concentration the ecosystem will support, r is the phytoplankton growth rate, and t is the elapsed time.

Mechanistic models were written in Excel software and parameter estimates were generated by minimization of least-square difference between chlorophyll data and model predictions. Statistical analysis were conducted according to Sokol and Rohlf (1995).

Results and Discussion

The San Joaquin River is located in the Central Valley of California, one of the most productive agricultural regions in the world. The San Joaquin Valley has a Mediterranean climate characterized by a dry-season (May through October) and a wet-season (November through April). In June and July, there is typically no measurable precipitation in the Central Valley. Air temperatures are typically mild in the winter (average low temperature of 2.6 °C in December) and hot in the summer (average high

temperature of 35 °C in July). In the dry season, most days are clear, there is little fog, and available sunlight is directly related to day-length. Agricultural production is highly dependent on irrigation and the summer months are commonly referred to as the “irrigation season.” Irrigation return flows are a significant source of nutrients to the San Joaquin River, which is the major drainage for the region (Figure 1).

The San Luis Drain (SLD) is a major tributary to the San Joaquin River above its confluence with the Merced River (Figure 1). The 43 km SLD drains a watershed of approximately 97,000 acres of irrigated farmland located in seven drainage and irrigation districts. The SLD discharges to Mud Slough, approximately 5 km above its confluence with the San Joaquin River. The soils in the SLD drainage are of marine origin and contain high concentrations of salts and trace elements (Gronberg et al., 1998). There has been a long-term interest in the water-quality of this region, consequently drainage flows in the SLD are accurately measured and several studies have examined the water quality of the SLD (Kratzer and Shelton, 1998; Kratzer et al., 2004; Stringfellow and Quinn, 2002). Previous studies showed that chlorophyll concentrations at the end of the SLD are consistently high in the summer months and that there is significant phytoplankton growth occurring in the SLD between the entrance and exit of the drain (Stringfellow and Quinn, 2002).

The SLD is an open, shallow, concrete lined channel. During the dry season, the flow in the SLD consists entirely of agricultural drainage and inlet and outlet flows approximately balance. Flows between May and September average $1.22 \text{ m}^3 \text{ sec}^{-1}$ and are consistent from year to year. In October, irrigation-return flows decline significantly and flows typically remain low throughout the wet season, except during periods of rainfall. Groundwater can enter the SLD through weep-valves, so during the wet-season exit flows may exceed input flows (data not shown).

The configuration of the SLD makes it an ideal location for meso-scale field experiments examining phytoplankton biokinetics. The SLD has no shading and is therefore fully exposed to sunlight and warm temperatures. The SLD does not support littoral plant or algal communities and all primary production in the drain is planktonic. After the first 2 km, the SLD has a uniform trapezoid shape and a consistent water depth of approximately 2.4 meters. During the summer, the hydraulic residence time of the SLD is approximately four days. The SLD contains a series of check structures at an average interval of 2.2 km. At these check structures, water drops approximately 0.5 meters and is passed through a culvert, which results in a complete mixing of the water at each structure. The uniformity of construction, flows, residence time, and depth, combined with regular mixing and resuspension of materials, allows modeling of the SLD as a complete mix, plug-flow reactor.

Phospholipid analysis shows the phytoplankton community in the SLD is dominated by diatoms (Figure 2) and that algae biomass consistently accounted for approximately 90% of the suspended biomass found at the exit of the channel, with the balance attributable to bacterial and fragments of higher plants. Diatoms were consistently 80% of the algal community, with green algae and dinoflagellates representing 15% and 5% respectively (Figure 2). The community structure was stable as biomass accumulate in the channel (data not shown) and the community structure is stable over time (Figure 2), supporting the conclusion that the SLD can be modeled as a pseudo-steady-state, plug flow reactor.

Measurement of nutrients and other water quality parameters were made at the head of the SLD in May, June, and July of 2003; June and July of 2004; and January of 2005 (Table 1). The water entering the SLD is a nutrient rich media entirely suited for algal growth. Over six years of records of water quality measurements at the terminus of the drain are also available (Kratzer et al., 2004; Stringfellow and Quinn, 2002). In all cases where nitrate was measured at the terminus of the drain during the dry-season months nitrate-N concentrations were above 8 mg L^{-1} , with the exception of one measurement in October where the nitrate-N was 4 mg L^{-1} . These reported $\text{NO}_3\text{-N}$ concentrations are over 50 times average reported phytoplankton half-saturation constants for nitrogen (Bowie et al., 1984). Available silicon concentrations at the exit of the channel were 20 to 200 times diatom half-saturation constants (Dahlgren, personal communication). Total phosphorous concentrations were also high at the exit of the SLD, consistently being greater than 0.02 mg L^{-1} as P (Kratzer et al., 2004; Stringfellow and Quinn, 2002), but outlet concentrations are significantly lower than measured inlet concentrations (Table 1), suggesting a significant phosphorous demand in the system. Total phosphorous concentrations at the outlet were still greater than or equal to reported half-saturation constants for phosphorous (Bowie et al., 1984). These results suggest that nitrogen and silicon are not limiting in this system, but that phosphate limitation could not be ruled out, despite the high phosphorous concentrations entering the SLD.

During the May and January studies, phytoplankton growth rates appeared exponential for the entire length of the channel and it was not apparent that algae growth ever reached the maximum carrying capacity of the system (data not shown). In contrast, the June and July studies demonstrated a biomass accumulation pattern consistent with limited growth kinetics (Figure 3). The consistency of results between years suggests that in June and July environmental conditions in the channel are sufficiently stable that pseudo-steady state conditions exist. The channel demonstrated a consistent pattern of sediment loss and phytoplankton accumulation as a function of residence time during June and July (Figures 3 and 4). Total phosphorous and soluble ortho-phosphate (oP) also typically demonstrated decline with residence time (Figure 5), but total phosphorous and oP concentrations were not significantly related to sediment concentrations ($r^2 < 0.060$). Agreement between phytoplankton growth patterns between different days and different years confirms that the SLD can be analyzed as a plug-flow reactor.

The logistic population model was fit to the June and July data and it was shown that the model gave an accurate description of the observed algal growth data (Figure 3). Biokinetic parameter estimates generated for individual data sets using the logistic model are shown in Table 2. The June and July data were directly comparable and showed surprising homogeneity year to year. The analysis of this system using the logistic model suggests that algae reach a maximum carrying capacity (K) in this system and that the maximum amount of algae biomass that can be supported on this drain water corresponds to less than $200 \mu\text{g L}^{-1}$ of chlorophyll-*a*.

The logistic model describes how a populations may respond to growth limiting conditions, however the model provides no mechanistic explanation as to what factors are limiting growth. As the phytoplankton population was shown to reach a maximum carrying capacity in this system, it was hypothesized that mechanisms controlling

phytoplankton biokinetics could be evaluated and further analysis was conducted to determine limiting factors.

The importance of light availability as a limiting factor for phytoplankton growth in the SLD was investigated. Although volatile suspended solids (VSS) concentrations increase as a function of residence time due to algae growth (Figure 3), total suspended solids and mineral solid concentrations decline along the length of the drain, due to settling losses (Figure 4). The removal of mineral solids has a more significant effect on light attenuation than the increase in algal biomass and as a result the depth of the photic zone increases as a function of residence time in the drain (Figure 6). An examination of observed growth rates (μ) demonstrates that the highest growth rates are typically observed in the first 40 hours of residence, in zones of higher turbidity (Figures 3 and 6). Additionally, incident solar radiation averaged 720 ± 64 langley's per day (approximately $138 \text{ E/m}^2 \text{ day}$) during the study period, which is well above reported saturating light intensities (Bowie et al., 1984; Knowlton and Jones, 1995; 1996; Sellers and Bukaveckas, 2003). Since the depth of the SLD is uniform after the first 2 km, the observation that photic zone is not correlated positively with algal growth rates is direct evidence that self-shading and light limitation are not controlling growth yields of phytoplankton in the SLD.

Analysis was conducted to determine if biomass yield correlated with initial conditions or changes in water chemistry between initial and final conditions. When both summer and winter data sets were included, yield was significantly correlated ($r > 0.900$, $\alpha = 0.05$) with seasonal factors (temperature, day length and day of year). Biomass yield had a significant correlation ($\alpha = 0.05$) with inoculum (initial phytoplankton) concentration ($r = 0.859$), electrical conductivity (-0.740), and changes in soluble o-phosphate (-0.977), turbidity (-0.813), and mineral solids (-0.708), but not initial ortho-phosphate concentration or change in total phosphorous concentration. There was significant correlation among independent variables and many chemical parameters varied with seasonal parameters (data not shown). The correlation between independent parameters in flowing systems limits the ability of statistical methods to identify factors limiting phytoplankton yields and growth rates. To address the limits of the statistical methods, a mechanistic approach to determining limiting factors was applied.

A mechanistic model was used to interpret the field data and evaluate the influence of light, pH, inorganic carbon, nutrient concentration, and mineral availability on algae growth in the SLD. Nitrogen, and silica were not included in the model, since direct measurements demonstrated they were not limiting in this system. Light and temperature were highly correlated and light was not modeled as an independent parameter. The mechanistic model was written using the minimum formulation approach (Bowie et al. 1985):

$$X_2 = X_1 e^{(\mu+g)(t_2-t_1)} \quad \text{Eq. 3}$$

$$\mu = f(T)f(L)\mu_{\max} \quad \text{Eq. 4}$$

$$g = f(T)f(Z)g_{\max} \quad \text{Eq. 5}$$

$$f(T) = 2^{(0.138(T-26))} \quad \text{Eq. 6}$$

$$f(L) = \min[f(M), f(P), f(C)] \quad \text{Eq. 7}$$

$$f(M) = \frac{M}{M + K_{sm}} \quad \text{Eq. 8}$$

$$f(P) = \frac{P}{P + K_{sp}} \quad \text{Eq. 9}$$

$$f(C) = \frac{C}{C + K_{sc}} \quad \text{Eq. 10}$$

$$C = \left(\frac{[H^+]^2}{[H^+]^2 + [H^+]10^{-6.4} + 10^{-16.7}} \right) 100 \quad \text{Eq. 11}$$

$$f(Z) = \frac{X_1}{X_1 + K_{sz}} \quad \text{Eq. 12}$$

where X_1 equals initial biomass at time 1 (t_1) measured as chlorophyll a , X_2 equals biomass at time 2 (t_2) measured as chlorophyll a , μ is the algal growth rate, g is the rate of algal grazing (negative number describing algal loss due to grazing). The observed growth rate, μ , is a function of the inherent maximum growth rate (μ_{max}), temperature (T), and the most severely limiting factor of either mineral solids concentration (M), carbon dioxide expressed as a percent of total dissolved inorganic carbon (C), or ortho-phosphate (P) concentration. This model uses suspended mineral solids as a bulk measure of undissolved nutrients and trace minerals, including silica and iron. The temperature modification factor ($f(T)$) was developed from the Arrhenius equation using observed maximum growth rates calculated by the logistic method as described above. Other factors are based on the Michaelis-Menten relationship (Bowie et al., 1984), where K_{sm} , K_{sp} , K_{sc} , and K_{sz} are the half-saturation constants for minerals, soluble ortho-phosphate (as P), carbon dioxide, and grazing, respectively. The observed grazing rate, g , is a function of the inherent maximum zooplankton grazing rate (g_{max}), temperature, and the density of algal biomass (X_1) as measured by chlorophyll a .

Data was fit to the model using a least squares approach and the best fit estimates for biokinetic parameters are presented in Table 3. Regression between the predicted and actual values, using the parameters listed in Table 3, yields an r^2 of 0.956 (Figure 7), suggesting the model provides an excellent description of phytoplankton growth in the SLD. The best fit estimate for μ_{max} is consistent with maximum values for r estimated using the logistic model (Table 2). These estimates of μ_{max} are consistent with previously reported values for diatoms (Bowie et al., 1984; Litchman et al., 2003).

Phytoplankton growth in the drain can be described as a function of phosphate concentration, mineral solids concentration, carbon dioxide solubility, and grazing pressures (Figure 8). When μ was less than μ_{max} , 61% of the time phytoplankton growth rate was limited by nutrient availability and 39% of the time by carbon dioxide availability. Of the times when nutrients were limiting growth rates, minerals were more limiting than phosphate 59% of the time. The K_{sp} of ortho-phosphate is estimated to be 0.012 mg L^{-1} as P, which is within the range of previously reported values (Bowie et al., 1984).

Carbon dioxide limitation of growth rate occurred at pH values as low as 8.1 during periods of rapid growth. The half-saturation constant for inorganic carbon (K_{sc}), expressed as a percent of total inorganic carbon in Table 3, is equivalent to 0.03 to 0.05 mg L^{-1} of C, assuming at least 50% of the alkalinity is due to carbonate buffering. This is a reasonable estimate for K_{sc} and is comparable to previously reported values (Bowie et al., 1984).

The stimulation of diatom growth by suspended mineral solids has not been demonstrated previously, but previous research supports the concept that suspended sediments can serve as reservoirs for both micro- and macronutrients and support algal growth processes. Sediments control the bioavailability nutrients and trace metals in a wide variety of aquatic systems (Cugier et al., 2005; Ellison and Brett, 2006; Garnier et al., 2005; Simpson et al., 2004; Steveninck et al., 1992; Wu and Chou, 2003). It has been frequently observed that sediment concentrations, nutrient concentrations, and phytoplankton growth yield are often correlated (e. g. Jones and Knowlton, 2005). Results from investigations of phytoplankton blooms in the Rhine and Marne Rivers suggest that during periods of rapid algal growth, soluble nutrients become limiting and the rate of algal growth is dependent on dissolution of nutrients from suspended particles in the water column (Garnier et al., 2005; Steveninck et al., 1992). Our analysis shows a positive relation between suspended mineral solids concentration and phytoplankton growth rate, indicating that suspended mineral solids are positive influence on phytoplankton growth in the SLD. This result is a significant departure from current thinking on the issue, since suspended mineral solids typically are expected to inhibit algal growth (via light attenuation), not act as a stimulant to algal growth.

In this system, mineral solids are believed to be functioning as a reservoir for a number of trace minerals required by algae. There is a correlation between mineral solids concentrations and total iron in river sediments collected in this region ($r^2 = 0.786$) and other trace metals and silica are also associated with sediments in riverine ecosystems (Garnier et al., 2005; Simpson et al., 2004; Steveninck et al., 1992; Wu and Chou, 2003). Suspended mineral solids may be acting as reservoirs for the dissolution of trace nutrients as rapid phytoplankton growth depletes available (soluble) nutrients in the water column. Dissolution limited growth has been observed in bacteria which grown on poorly soluble compounds (Grimberg et al., 1994; Grimberg et al., 1996) and a similar phenomena could explain the dependence of algal growth on suspended mineral particles. The stimulatory effect of sediments on plankton algae, particularly diatoms, also makes sense in that the presence of suspended sediments and associated high turbidity would prevent the growth of benthic plants or algae, benefiting planktonic algal population in the competition for

limit ecological resources. The stimulatory effect of sediments on phytoplankton growth is under further investigation.

Biomass yield (carrying capacity) is limited by a combination of phosphate depletion and zooplankton grazing. A density dependent decay component is needed to describe the decline of algae biomass observed at the end of the drain, which typically begins after sixty hours of residence time in the drain (Figure 8). The decline in biomass could not be characterized using a fixed intrinsic decay constant or settling function to describe algal losses (data not shown). The maximum grazing rate estimated by the model is high (Table 3), but the K_{sz} suggested that the process is not particularly efficient, which would suggest that the grazing impact would be from zooplankton rather than benthic bivalves. This is consistent with field observations. The concrete lined channel is inhospitable to benthic organisms, but a fish population is present in the last 16 kilometers of the SLD, suggesting a significant food web is present. Direct measurements of zooplankton were not included in this study, but will be made in future investigations.

Conclusions

The SLD was an ideal system to study factors limiting phytoplankton growth in eutrophic rivers. The hydraulic simplicity of the system allowed the modeling of the system as a plug-flow reactor and excess sunlight allowed phytoplankton to reach their maximum carrying capacity in the study reach, despite very high initial nutrient conditions. The attainment of limited growth conditions in the presence of excess light and nitrogen allowed the direct measurement of other limiting factors in this highly eutrophic system. The use of a mechanistic model provided insight into how statistically correlated factors were influencing phytoplankton biokinetics in a highly eutrophic system. The analysis using the mechanistic model showed that mineral solids were serving as a source of nutrients for the diatom dominated system, that high growth rates occurred in conjunction with high sediment concentrations, and that periods of rapid growth could result in a carbon dioxide limitation. Overall, soluble ortho-phosphate was still associated with limits to growth yield, but grazing pressures reduced phytoplankton standing crop after maximum yield had been reached. The ability of sediments to stimulate phytoplankton growth has not been previously shown. The applicability of these findings to phytoplankton growth in the San Joaquin River and the role on sediments in the biokinetic stimulation of phytoplankton populations will be further investigated.

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References

- American Public Health Association (1998) Standard Methods for the Examination of Water and Wastewater, American Public Health Association, Washington, D.C.
- Becker, C., Feuchtmayr, H., Brepohl, D., Santer, B. and Boersma, M. (2004) Differential impacts of copepods and cladocerans on lake seston, and resulting effects on zooplankton growth. *Hydrobiologia* 526(1), 197-207.
- Billen, G., Garnier, J., Ficht, A. and Cun, C. (2001) Modeling the response of water quality in the Seine river estuary to human activity in its watershed over the last 50 years. *Estuaries* 24(6B), 977-993.
- Bowie, G.L., Mills, W.B., Donald B. Porcella, Campbell, C.L., Pagenkopf, J.R., Rupp, G.L., Johnson, K.M., Chan, P.W.H., Gherini, S.A. and Chamberlin, C.E. (1984) Rates, Constants, and Kinetics Formulations in Surface Water Modeling, Second Edition., Environmental Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Athens, GA.
- Cerco, C.F. and Noel, M.R. (2004) Process-based primary production modeling in Chesapeake Bay. *Marine Ecology-Progress Series* 282, 45-58.
- Cugier, P., Billen, G., Guillaud, J.F., Garnier, J. and Menesguen, A. (2005) Modeling the eutrophication of the Seine Bight (France) under historical, present and future riverine nutrient loading. *Journal of Hydrology* 304(1-4), 381-396.
- Ellison, M.E. and Brett, M.T. (2006) Particulate phosphorus bioavailability as a function of stream flow and land cover. *Water Research* 40(6), 1258-1268.
- Galois, R., Richard, P. and Fricourt, B. (1996) Seasonal variations in suspended particulate matter in the Marennes-Oleron Bay, France using lipids as biomarkers. *Estuarine, Coastal and Shelf Science* 43, 335-357.
- Garnier, J., Nemery, J., Billen, G. and Thery, S. (2005) Nutrient dynamics and control of eutrophication in the Marne River system: modeling the role of exchangeable phosphorus. *Journal of Hydrology* 304(1-4), 397-412.
- Grimberg, S.J., Aitken, M.D. and Stringfellow, W.T. (1994) The influence of a surfactant on the rate of phenanthrene mass-transfer into water. *Water Science and Technology* 30(7), 23-30.
- Grimberg, S.J., Stringfellow, W.T. and Aitken, M.D. (1996) Quantifying the biodegradation of phenanthrene by *Pseudomonas stutzeri* P16 in the presence of a nonionic surfactant. *Applied and Environmental Microbiology* 62(7), 2387-2392.
- Gronberg, J.A., Dubrovsky, N.M., Kratzer, C.R., Domagalski, J.L., Brown, L.R. and Burow, K.R. (1998) Environmental Setting of the San Joaquin-Tulare Basins, California. WRI 97-4205, US Geological Survey, Sacramento, CA.
- Guckert, J.B., Antworth, C.P., Nichols, P.D. and White, D.C. (1985) Phospholipid, ester-linked fatty-acid profiles as reproducible assays for changes in prokaryotic community structure of estuarine sediments. *Fems Microbiology Ecology* 31(3), 147-158.
- Hagy, J.D., Boynton, W.R., Keefe, C.W. and Wood, K.V. (2004) Hypoxia in Chesapeake Bay, 1950-2001: Long-term change in relation to nutrient loading and river flow. *Estuaries* 27(4), 634-658.

- Haider, S., Naithani, V., Viswanathan, P.N. and Kakkar, P. (2003) Cyanobacterial toxins: a growing environmental concern. *Chemosphere* 52(1), 1-21.
- Hilton, J., O'Hare, M., Bowes, M.J. and Jones, J.I. (2006) How green is my river? A new paradigm of eutrophication in rivers. *Science of the Total Environment* 365, 66-83.
- Hutchins, G. (1973) Eutrophication. *American Scientist* 61(3), 269-279.
- Jassby, A. and Nieuwenhuyse, E.E.V. (2005) Low dissolved oxygen in an estuarine channel (San Joaquin River, California): mechanisms and models based on long-term time series. *San Francisco Estuary and Watershed Science* 3(2).
- Jones, J.R. and Knowlton, M.F. (2005) Suspended solids in Missouri reservoirs in relation to catchment features and internal processes. *Water Research* 39(15), 3629-3635.
- Jorgensen, S.E. (1976) A eutrophication model for a lake. *Ecological Modelling* 2, 147-165.
- Knowlton, M.F. and Jones, J.R. (1995) Temporal and spatial dynamics of suspended sediment, nutrients, and algal biomass in Mark Twain Lake, Missouri. *Archiv Fur Hydrobiologie* 135(2), 145-178.
- Knowlton, M.F. and Jones, J.R. (1996) Experimental evidence of light and nutrient limitation of algal growth in a turbid midwest reservoir. *Archiv Fur Hydrobiologie* 135(3), 321-335.
- Koch, R.W., Guelda, D.L. and Bukaveckas, P.A. (2004) Phytoplankton growth in the Ohio, Cumberland and Tennessee Rivers, USA: inter-site differences in light and nutrient limitation. *Aquatic Ecology* 38(1), 17-26.
- Koelmans, A.A., Van der Heijde, A., Knijff, L.M. and Aalderink, R.H. (2001) Integrated modelling of eutrophication and organic contaminant fate and effects in aquatic ecosystems. A review. *Water Research* 35(15), 3517-3536.
- Kratzer, C.R. and Shelton, J.L. (1998) Water Quality Assessment of the San Joaquin-Tulare Basins, California: Analysis of Available Data on Nutrients and Suspended Sediment in Surface Water, 1972-1990. USGS (ed).
- Kratzer, C.R., Dileanis, P.D., Zamora, C., Silva, S.R., Kendall, C., Bergamaschi, B.A. and Dahlgren, R.A. (2004) Sources and Transport of Nutrients, Organic Carbon, and Chlorophyll-a in the San Joaquin River Upstream of Vernalis, California, during Summer and Fall, 2000 and 2001. WRI 2003-4127., U.S. Geological Survey, Sacramento, CA.
- Kuoppo, P., Autio, R., Kuosa, H., Setälä, O. and Tanskanen, S. (1998) Nitrogen, silicate and zooplankton control of the planktonic food-web in spring. *Estuarine, Coastal, and Shelf Science* 46(1), 65-75.
- Levin, G.V. (1967) New pollution - urbanization increased use of fertilizers and detergents and paradoxically advances in wastewater treatment are accelerating problem of eutrophication. *Civil Engineering* 37(5), 68-&.
- Litchman, E., Steiner, D. and Bossard, P. (2003) Photosynthetic and growth responses of three freshwater algae to phosphorus limitation and daylength. *Freshwater Biology* 48, 2141-2148.

- Muller-Solger, Jassby, A.D. and Muller-Navarra, D.C. (2002) Nutritional quality of food resources for zooplankton (*Daphnia*) in a tidal freshwater system (Sacramento-San Joaquin River Delta). *Limnology and Oceanography* 47(5), 1468-1476.
- Nichols, P.D., Guckert, J.B. and White, D.C. (1986) Determination of Monounsaturated Fatty-Acid Double-Bond Position and Geometry for Microbial Monocultures and Complex Consortia by Capillary Gc-MS of Their Dimethyl Disulfide Adducts. *Journal of Microbiological Methods* 5(1), 49-55.
- Nikolaou, A.D. and Lekkas, T.D. (2001) The role of natural organic matter during formation of chlorination by-products: A review. *Acta Hydrochimica Et Hydrobiologica* 29(2-3), 63-77.
- Nyholm, N. (1978) A simulation model for phytoplankton growth and nutrient cycling in eutrophic, shallow lakes. *Ecological Modeling* 4, 279-310.
- Parr, L.B. and Mason, C.F. (2004) Causes of low oxygen in a lowland, regulated eutrophic river in Eastern England. . *The Science of the Total Environment* 321(1-3), 273-286.
- Pers, B.C. (2005) Modeling the response of eutrophication control measures in a Swedish lake. *Ambio* 34(7), 552-558.
- Plus, M., La Jeunesse, I., Bouraoui, F., Zaldivar, J.M., Chapelle, A. and Lazure, P. (2006) Modelling water discharges and nitrogen inputs into a Mediterranean lagoon - Impact on the primary production. *Ecological Modelling* 193(1-2), 69-89.
- Robson, B. (2005) Representing the effects of diurnal variations in light on primary production on a seasonal time-scale. *Ecological Modelling* 186(3), 358-365.
- Scavia, D. and Bricker, S.B. (2006) Coastal eutrophication assessment in the United States. *Biogeochemistry* 79(1-2), 187-208.
- Sellers, T. and Bukaveckas, P.A. (2003) Phytoplankton production in a large, regulated river: A modeling and mass balance assessment. *Limnology and Oceanography* 48(4), 1476-1487.
- Simpson, S.L., Angel, B.M. and Jolley, D.F. (2004) Metal equilibration in laboratory-contaminated (spiked) sediments used for the development of whole-sediment toxicity tests. *Chemosphere* 54, 597-609.
- Sladeckova, A. (1998) Green algae in water supplies: a review. *Biologia* 53(4), 557-565.
- Sokal, R.R. and Rohlf, F.J. (1995) *Biometry: The Principles and Practice of Statistics in Biological Research*, W. H. Freeman & Co., New York, NY.
- Steveninck, E.D.d.R.v., Admiraal, W., Breebaart, L., Tubbing, G.M.J. and Zanten, B.v. (1992) Plankton in the River Rhine: structural and functional changes observed during downstream transport. *Journal of Plankton Research* 14(10), 1351 - 1368.
- Stringfellow, W.T. and Quinn, N.W.T. (2002) Discriminating Between West-Side Sources of Nutrients and Organic Carbon Contributing to Algal Growth and Oxygen Demand in the San Joaquin River. Ernest Orlando Lawrence Berkeley National Laboratory Formal Report No. LBNL-51166., Berkeley National Laboratory, Berkeley, CA.
- Wnorowski, A.U. (1992) Tastes and Odors in the Aquatic Environment - a Review. *Water Sa* 18(3), 203-214.

Wu, H.T. and Chou, T.L. (2003) Silicate as the limiting nutrient for phytoplankton in a subtropical eutrophic estuary of Taiwan. *Estuarine Coastal and Shelf Science* 58(1), 155-162.

Table 1: Water quality conditions for drainage entering the San Luis Drain during the study period. Data from January, May, June, and July 2003 to 2004 included (n = 6).

| Parameter | Mean | Minimum | Maximum |
|--|-------------|----------------|----------------|
| Flow (cfs) | 48.4 | 41.0 | 55.0 |
| Temp (deg C) | 20.9 | 9.3 | 26.9 |
| EC (millisemens cm⁻¹) | 4.842 | 4.190 | 6.414 |
| DO (%) | 112.8 | 96.5 | 152.5 |
| pH | 8.06 | 7.83 | 8.36 |
| Turbidity (NTU) | 77.9 | 33.4 | 155.0 |
| Dissolved organic carbon (mg L⁻¹) | 6.7 | 5.2 | 9.4 |
| Total organic carbon (mg L⁻¹) | 8.1 | 5.6 | 11.5 |
| Volatile suspended solids (mg L⁻¹) | 14.3 | 3.0 | 22.0 |
| Total suspended solids (mg L⁻¹) | 135.1 | 69.7 | 199.2 |

| Parameter | Mean | Minimum | Maximum |
|---|-------------|----------------|----------------|
| Mineral suspended solids (mg L⁻¹) | 120.9 | 59.0 | 177.2 |
| Nitrate-N (mg L⁻¹) | 12.9 | 9.4 | 16.4 |
| Soluble o-phosphate (mg L⁻¹) | 0.208 | 0.061 | 0.389 |
| Total phosphorous (mg L⁻¹) | 0.679 | 0.390 | 0.942 |
| Chlorophyll-a (µg L⁻¹) | 32.4 | 4.2 | 49.0 |
| Pheophytin (µg L⁻¹) | 9.5 | 3.1 | 11.4 |
| Chlorophyll-b (µg L⁻¹) | 1.8 | 1.2 | 2.8 |
| Xanthophyll (µg L⁻¹) | 1.2 | 0.6 | 1.8 |

Table 2: Best fit parameters for the logistic model (eq. 1) to observed algal growth patterns in the SLD.

| Date | Day of year | N_0 | K | r | r^2 |
|----------|-------------|----------------------------|----------------------------|------------------|-------|
| | | $\mu\text{g Chl-a L}^{-1}$ | $\mu\text{g Chl-a L}^{-1}$ | hr^{-1} | |
| 01/13/05 | 13 | 6.71 | 10.50 | 0.023 | 0.971 |
| 05/13/04 | 134 | 19.02 | 203.00 | 0.023 | 0.936 |
| 06/17/03 | 168 | 19.90 | 123.90 | 0.219 | 0.745 |
| 07/13/04 | 195 | 36.60 | 162.10 | 0.049 | 0.922 |
| 06/30/03 | 181 | 45.70 | 177.20 | 0.055 | 0.942 |
| 07/29/03 | 210 | 16.60 | 142.00 | 0.062 | 0.931 |

Table 3: Best fit estimates for parameters included in the mechanistic model for algal growth in the San Luis Drain. See text for explanation. Data from January, May, June, and July 2003 to 2004 included.

| Parameter | Best fit estimate | Units |
|-------------|-------------------|--|
| μ_{max} | 0.061 | hr ⁻¹ |
| g_{max} | -0.053 | hr ⁻¹ |
| K_{sm} | 19.3 | mg Mineral solids L ⁻¹ |
| K_{sp} | 0.009 | mg PO ₄ -P L ⁻¹ |
| K_{sc} | 0.25 | % H ₂ CO ₃ |
| K_{sz} | 100 | µg Chlorophyll-a L ⁻¹ |

Figure 1: Map of study area located in the San Joaquin Valley of California. The San Luis Drain is a concrete lined channel that conveys agricultural drainage from farms in the south, past sensitive wetland areas, and discharges into the San Joaquin River via Mud Slough. Measurements were made at the inlet and outlet and the 18 check structures along the length of the channel.

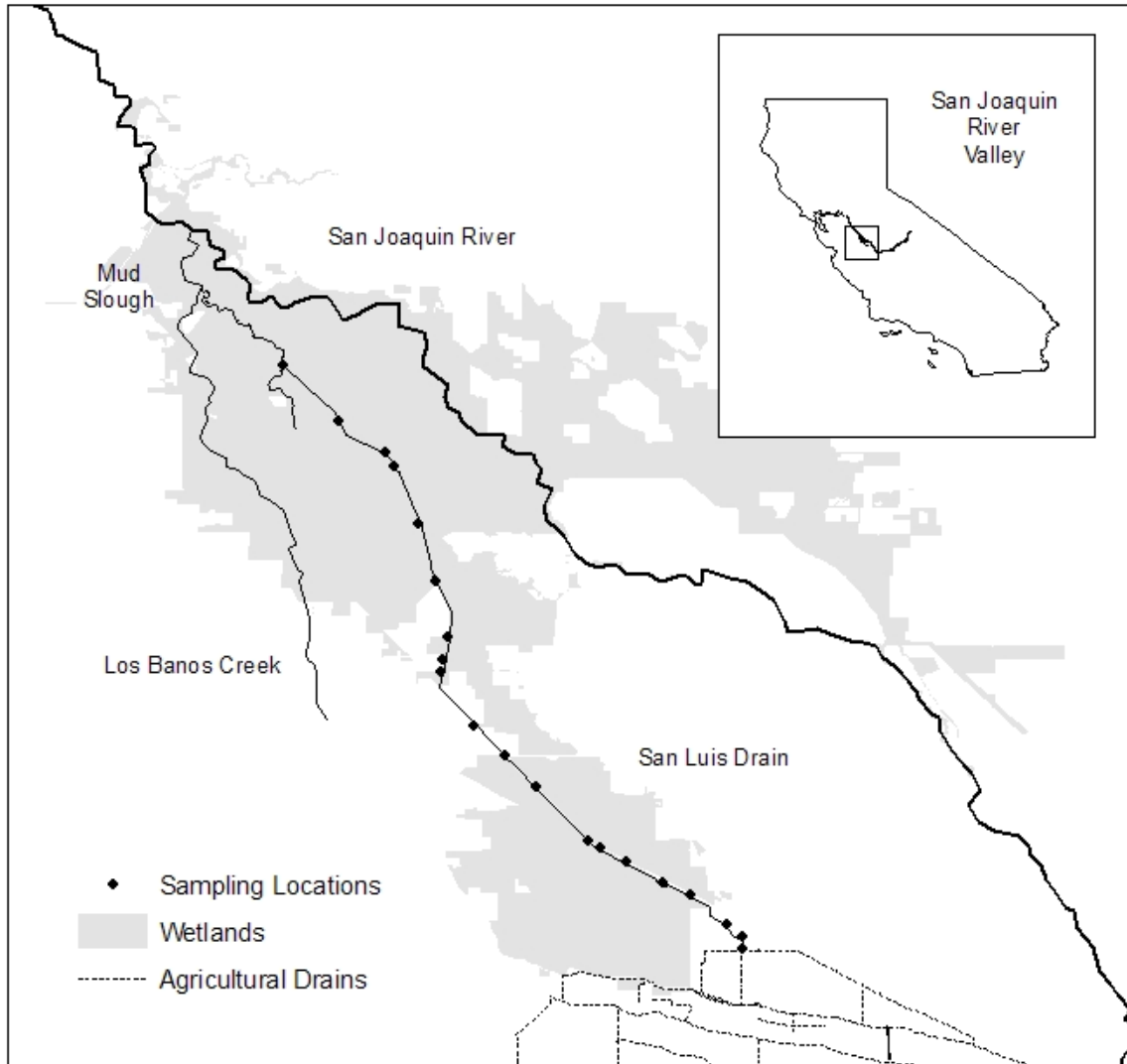


Figure 2: Community structure of biomass in the San Luis Drain as determined by phospholipid fatty acid analysis. The system is dominated by diatoms and exhibits a stable community structure. Data from 2005 shown.

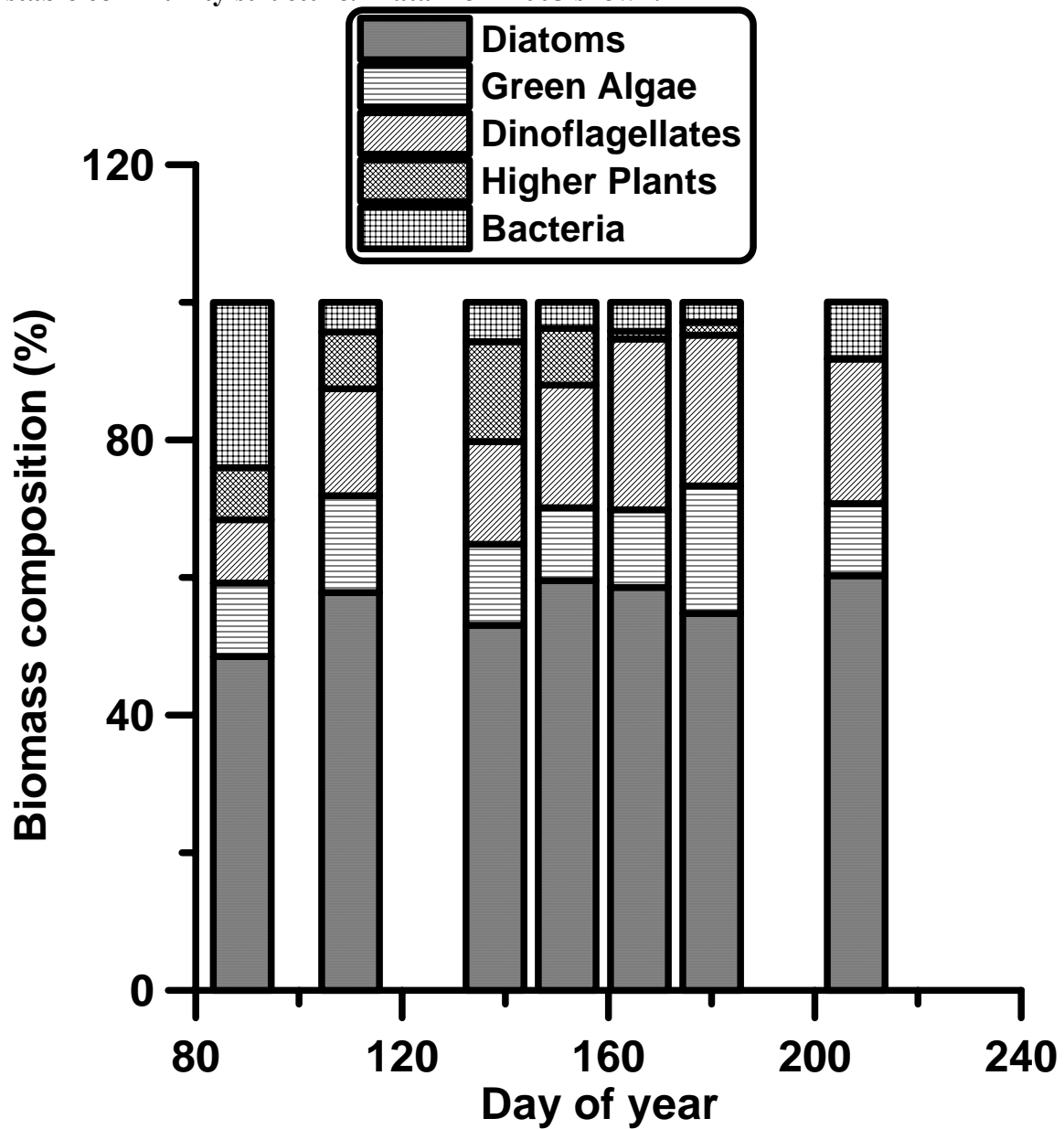


Figure 3: Phytoplankton concentration as a function of hydraulic residence time during June and July for the San Luis Drain. Mean and standard deviation for five surveys conducted between 2003 and 2005 with mean data fit using the logistic equation (eq 1).

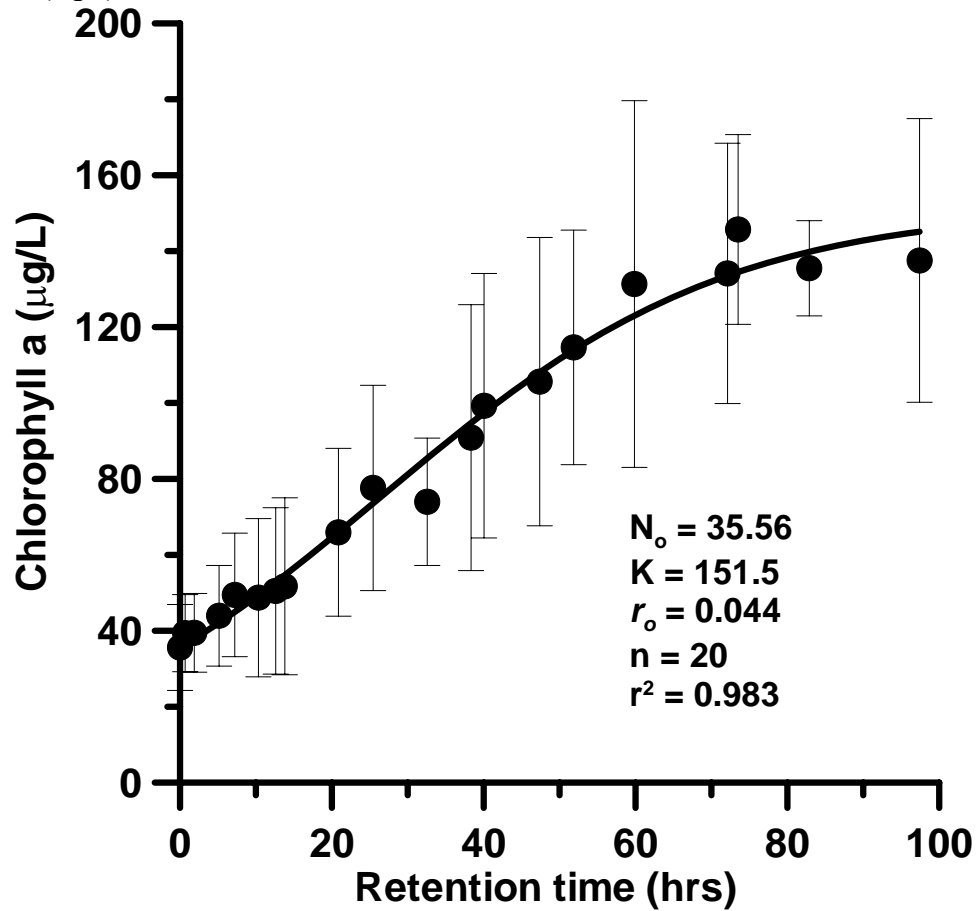


Figure 4: Sediment concentration as a function of hydraulic residence time during June and July for the San Luis Drain. Mean and standard deviation for four surveys conducted in 2003 and 2004.

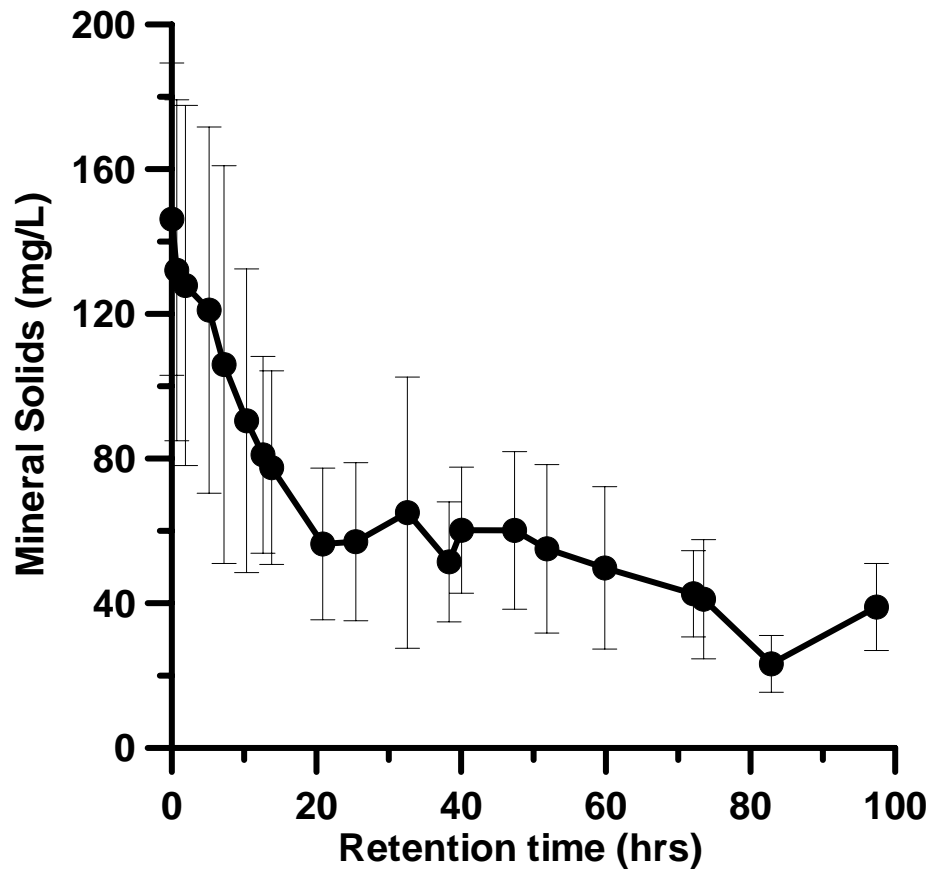


Figure 5: Phosphate concentration as a function of hydraulic residence time during June and July for the San Luis Drain. Mean and standard deviation for four surveys conducted in 2003 and 2004.

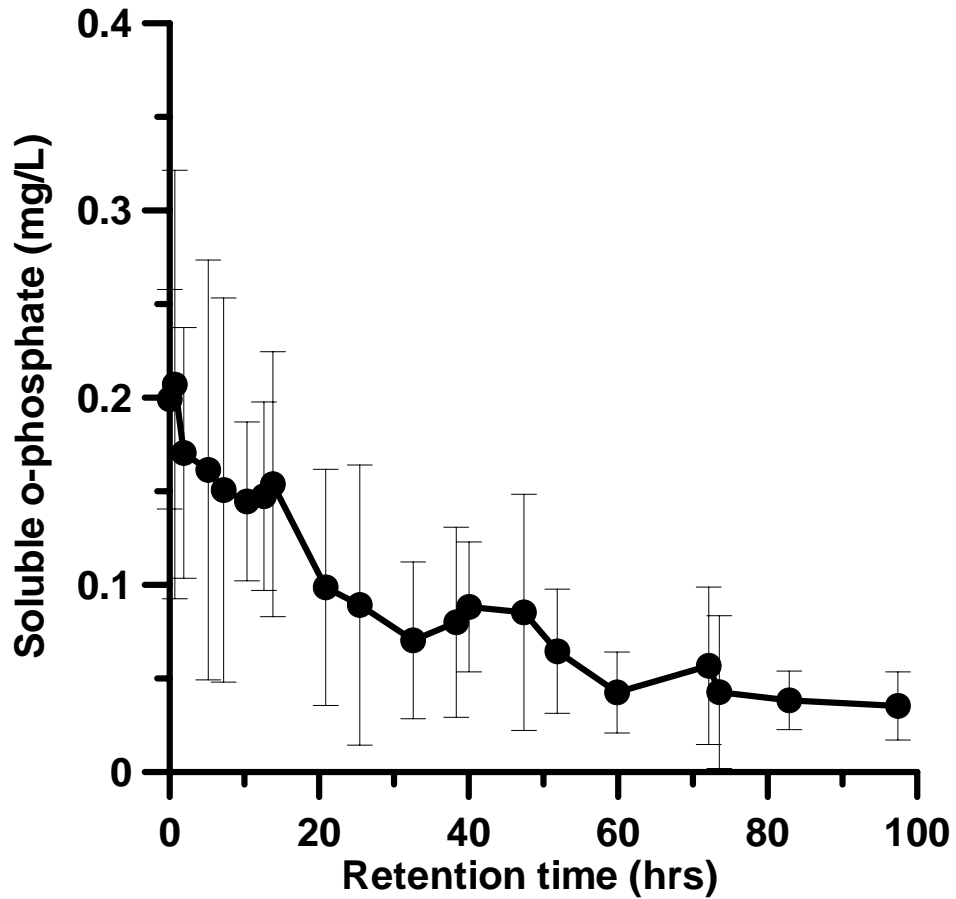


Figure 6: Depth of photic zone and observed phytoplankton growth rate as a function of hydraulic residence time during June and July for the San Luis Drain. Mean and standard deviation for four surveys conducted in 2003 and 2004. Linear least squares fit to all data, mean of all data shown.

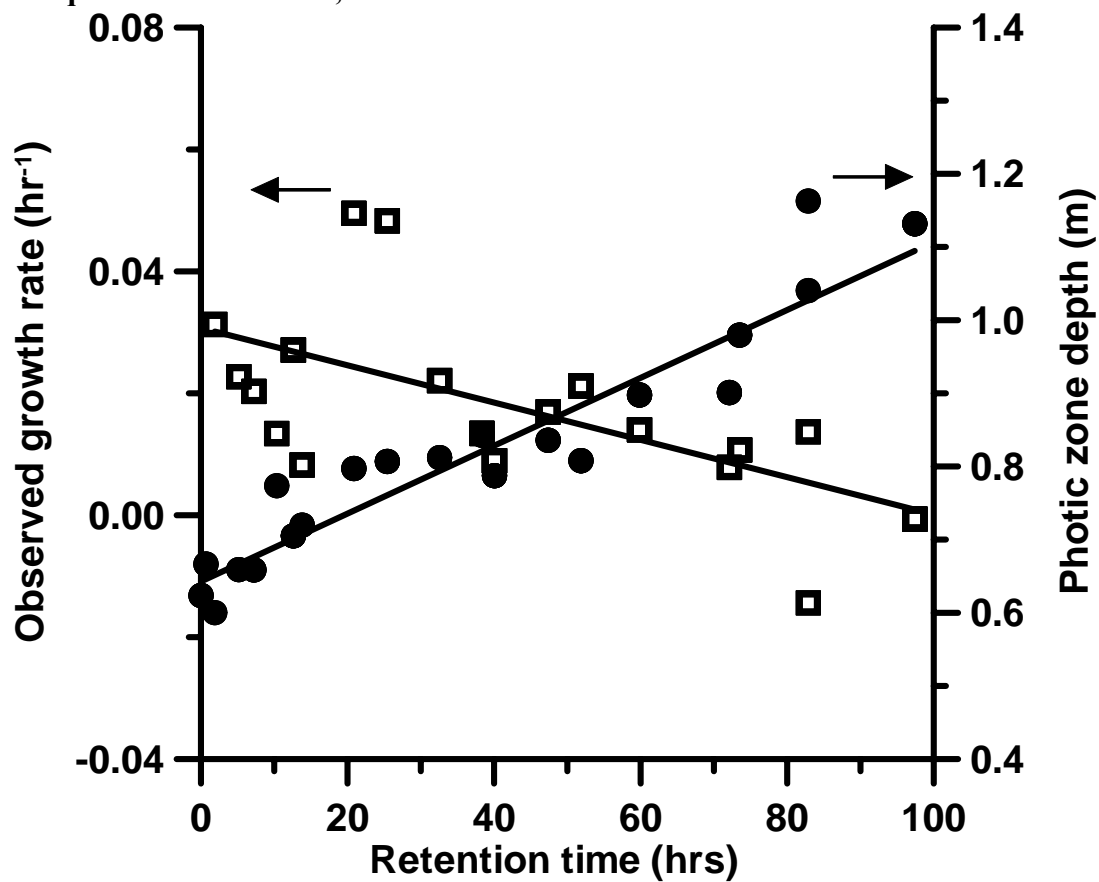


Figure 7: Mechanistic model fit to data using parameters in Table 3. Data for June and July 2003 and 2004.

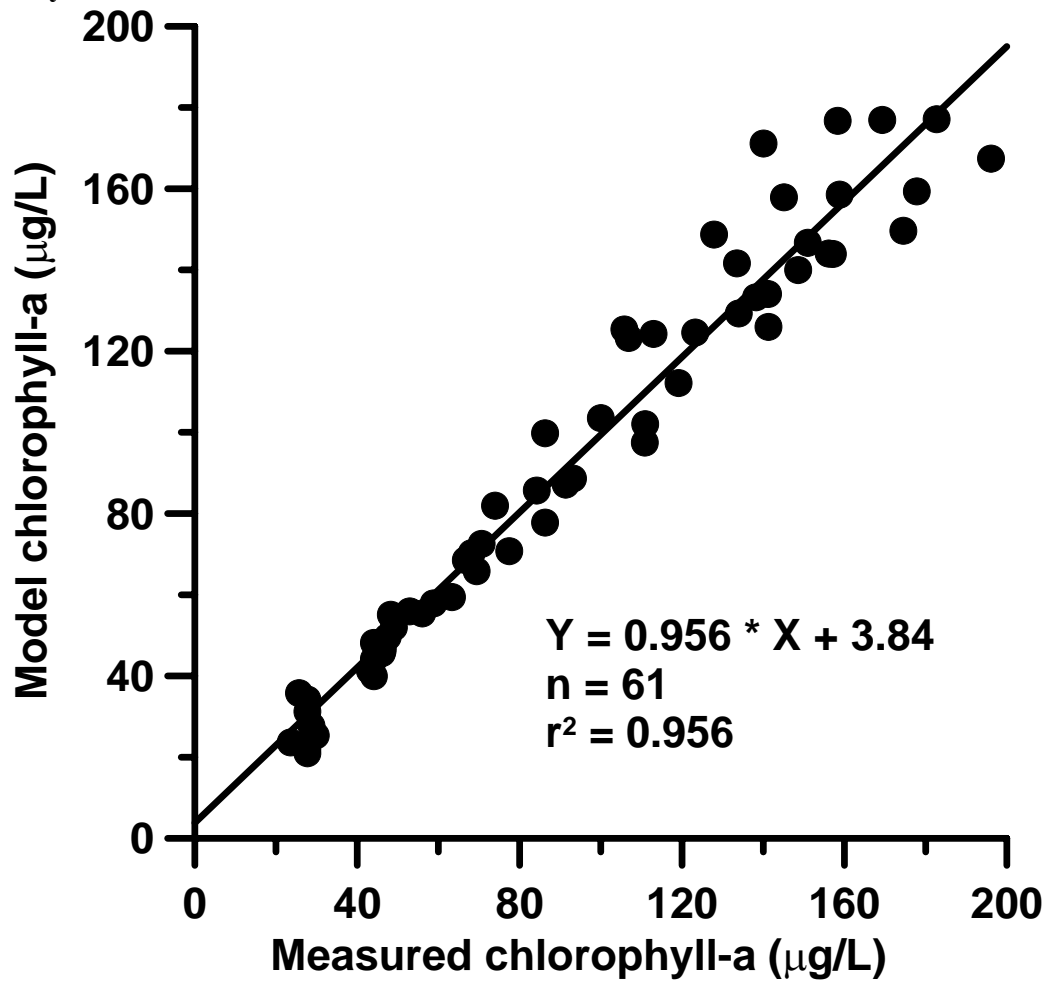


Figure 8: Model fit to data from July 13, 2004, showing decline in phytoplankton chlorophyll a at extended residence times attributed to zooplankton grazing by mechanistic model.

